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MECHANISMS OF REACTIONS OF OXIDIZERS

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## MECHANISMS OF REACTIONS OF OXIDIZERS

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The following publications have resulted during the past year from research under this contract:

- 1. "Ammonium Nitrate Explosive Compositions Containing (Metal-Excess Chloride) Combustion Catalyst". A. G. Keenan, Karl J. Notz, Jr., Nicholas B. Franco, U. S. Patent 3,336,171, August 15, 1967.
- 2. "Pyrex Membrane Potential in Binary Nitrate Melts". A. G. Keenan, K. Notz, and F. L. Wilcox. Journal of Physical Chemistry, 72 1085 (1968).
- 3. "Synergistic Catalysis of Ammonium Nitrate Decomposition". N. B. Franco, Ph.D. Dissertation, University of Miami, January 1968.
- 4. "Variations in Acidity and Water Content During the Chloride-Catalyized Decomposition of Ammonium Nitrate". Ronda W. Waldinger, M.S. Thesis, University of Miami, June 1967.
- 5. "The Synergistic Catalysis of Ammonium Nitrate Decomposition by Copper and Chloride Ions". J. W. Brockington, M.S. Thesis, University of Miami, August 1967.
- 6. "Electrometric Measurements in Fused Alkali Nitrates". Floyd L. Wilcox, M.S. Thesis, University of Miami, August 1967.

An invention report entitled "Synergistically Catalyzed Composite Oxidizer", A. G. Keenan and Robert Siegmund inventors, has been submitted to ONR on NAVEXOS Form 2374 and to Research Corporation acting as University patent agents. Counsel for Research Corporation has declared their opinion that the subject matter is patentably distinct from earlier claims under U. S. 3,336,171. A patent application is in preparation.

In current work on the contract, research is in progress on the kinetics of catalyzed ammonium perchlorate decomposition. The purpose is to determine if the principles of synergistic catalysis found for ammonium nitrate and its mixtures with ammonium perchlorate, can be applied to ammonium perchlorate alone. So fare,

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only one copper chloride catalyst has been studied in a preliminary way. Techniques and apparatus have, however, been developed which allow concordant activation energies to be determined in several ways for the same decomposition. The reaction parameters used include induction period, time to rate maximum, rate constants for the acceleratory and deceleratory parts of the rate curve and time between two arbitrary decomposition fractions. The various activation energies obtained are all within a few per cent of 30 kcal/mole for a single catalyst concentration. Measurements will be extended to cover a range of catalyst compositions and concentrations.

A second area of current research is directed toward establishing an acidity scale in fused salts for application toward the potentiometric study of the role of acidity in oxidizer decomposition mechanisms. Oxygen electrodes, platinum wire electrodes, Pyrex membranes and chromate-dichromate colorimetric indicators have been investigated. Work at present is concentrated on chromate indicators. Accurate values for the molal absorptivity coefficient of chromate ion in binary nitrate eutectic at 250° have been determined over a range of wavelengths. Similar measurements for dichromate ion are under way. These data will be combined with readings of an oxygen electrode to determine an equilibrium constant for the reaction of oxide ion with dichromate to form chromate.

Once the colorimetric and potentiometric methods of measuring acidity in fused salts have been developed, they will be applied to the elucidation of the preliminary correlations, previously reported, which have been observed between reaction rates in decomposing oxidizers and the emf's of various electrode pairs.

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13 ABSTRACT					
Progress during the year in	the investig	ations (	of the		
synergistically catalyzed de	composition	of oxid	dizers		
such as ammonium nitrate and	l ammonium pe	rchlor	ate is Gray		
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and electrometric measurements.					

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